THE PHOTO-OXIDATION OF CARBON TETRACHLORIDE

Thesis by

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In Partial Fulfillment of the Requirements

for the Degree of Master of Science

California Institute of Technology

Pasadena, California

1933.

The help, supervision, and inspiration given by Dr. R. G. Dickinson have made this work possible and are deeply appreciated.

THE PHOTO-OXIDATION OF CARBON TETRACHLORIDE.

When carbon tetrachloride is irradiated in an open vessel by ultra-violet light, a strong odor of phosgene develops; and if the liquid is then shaken with water, an acid solution results which will oxidize potassium iodide to iodine. Benrath and Hertel[1], and Mackenzie and King[2], attribute this to a photochemical decomposition:

$$2CCl_4 + h\nu \longrightarrow C_2Cl_6 + Cl_2$$

and Morton[3] and Dhar[4] agree; but this does not account for the formation of phosgene. Evidently, under these conditions there is an oxidation, possibly accompanied by a hydrolysis.

In order to clear up this point, and to study the behavior of carbon tetrachloride when illuminated by ultra-violet light,-- a subject of especial interest since carbon tetrachloride is used as a solvent in studying the photochemical reactions of other substances,-- the following experiments were undertaken.

A series of illuminations of carbon tetrachloride which had been dried and freed from

oxygen was made. Carbon tetrachloride absorbs continuously below about 2800 Ångstroms.[5] The light used was mainly the mercury resonance line, 2537 Ångstroms. When the carbon tetrachloride was sufficiently pure, no oxidizing power nor acidity were developed after a considerable illumination.

A second series of experiments was made with carbon tetrachloride saturated with oxygen. After the illuminated sample had been shaken with water, an oxidizing agent, an acid, and chloride ion were found to have been developed in approximately equivalent quantities. This suggests the reaction,

$$CCl_4 + \tfrac{1}{2} O_2 \longrightarrow COCl_2 + Cl_2$$

The quantum yield for this reaction was found to be two equivalents of products per quantum of light absorbed, or one molecule of carbon tetrachloride decomposed.

Experimental.

The sample of carbon tetrachloride was illuminated under as nearly as possible the same conditions as an actinometer. The quantum

yield of the actinometer reaction was known, and from this it was possible to calculate the amount of light which had been absorbed by the carbon tetrachloride. After the illumination, the sample was analyzed as described below.

The illuminations were carried out in a spherical quartz flask, four centimeters in diameter, with a neck eight millimeters in diameter and nine centimeters long. To this was sealed a pyrex glass gas reservoir, which took several forms as shown in Fig. 1. Fig. 1A shows the type which was used in all oxygen-free illuminations except run 47; for the latter run, the reservoir shown in Fig. 1C was used, together with a vacuum distillation to be described later. The seal was made by means of fused silver chloride between the two tightly-fitting surfaces, which had been previously platinized; and it was further protected by an outer seal of de Khotinsky cement.

The actinometer was placed in a similar flask. At first, the two ~~two~~ flasks were clamped about fifteen centimeters equidistant from the lamp, in roughly reproduceable positions; and their positions were alternated each ten minutes during

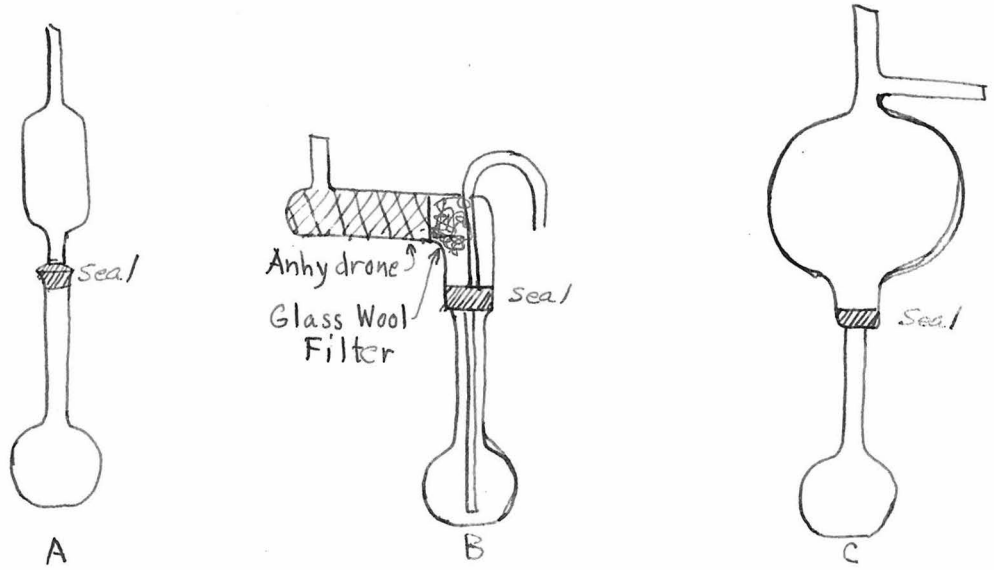
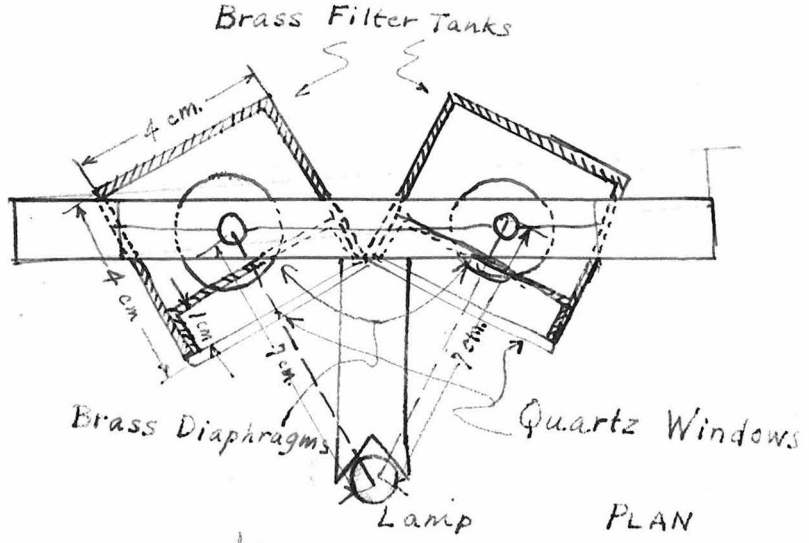


FIG. 1. REACTION FLASKS.



For the sake of clarity, the brass diaphragm in this tank is omitted

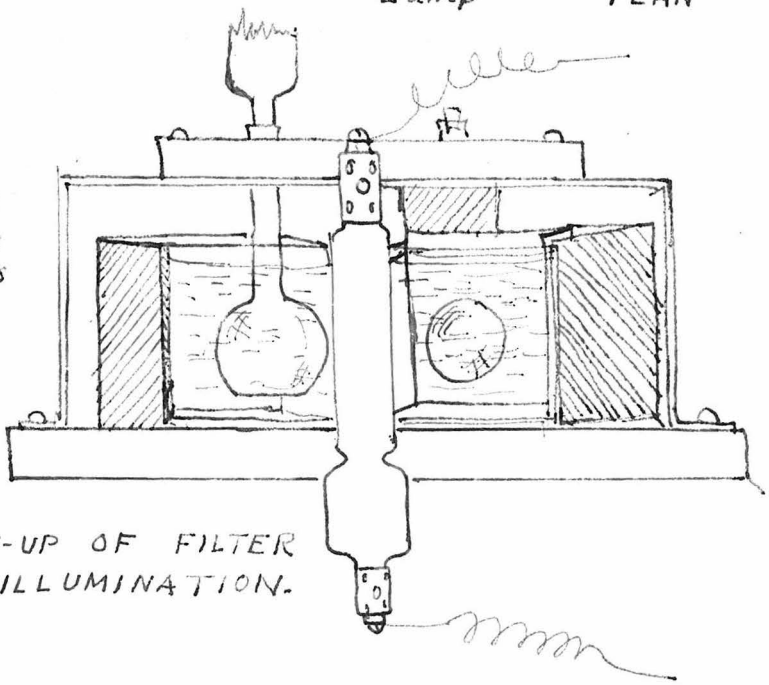


FIG. 2. SET-UP OF FILTER TANKS FOR ILLUMINATION.

the run. Tests made by illuminating the flasks when both were filled with actinometer solution showed that this gave an even illumination to each flask.

Beginning with run 10, a bracket was used to hold both flasks and the lamp in definite position, as well as small tanks of filter solution in which the flasks were submerged. See Fig. 2. The flasks had always the same face turned towards the lamp. It was inconvenient to change the positions of the flasks during a run; and a series of seven illuminations with actinometer in both flasks showed that the flask usually containing the carbon tetrachloride received 1.21 times as much light as did the actinometer flask. See Table 1. The figures given for the amount of light received have been corrected for this, where necessary.

Table 1. Actinometer in both flasks. Cc. of 0.05 n. $AgNO_3$ used to titrate the illuminated actinometer solutions.

Run	"Reaction flask"	"actinometer"	ratio
10a	1.47	1.76	1.20
19a	1.73	1.43	1.21
19b	1.29	1.07	1.21
47a	2.34	1.94	1.21
48	0.93	0.77	1.21
49	1.78	1.43	1.24
50	1.81	1.49	1.21

The filter solution was a 10% solution of sodium acetate. This solution transmits light of wavelengths as low as 2537 ångstroms, but absorbs almost all shorter wavelengths.[5] This was verified for the thickness and concentration used by means of a spectrophotograph. Carbon tetrachloride does not absorb much above 2537 ångstroms; nor does the actinometer react to light of much longer wavelength[7,8]. It was thus mostly 2537 ångstrom light which was effective.

The actinometer was a half-normal solution of monochloracetic acid. According to Rudberg[7], this solution absorbs over 90% of the 2530 ångstrom light in a layer two centimeters thick. The path of light through the spherical flasks used was limited by circular diaphragms to a thickness of at least three centimeters thick. Spectrophotographs showed practically complete absorption of the 2537 ångstrom line by carbon tetrachloride and chloracetic acid in the flasks.

The light absorbed by the actinometer causes a hydrolysis to occur:

$$CH_2Cl.COOH + H_2O \longrightarrow CH_2OH.COOH + HCl.$$

Rudberg gives a quantum yield within 7% of unity[7].

The extent of hydrolysis is determined by titrating the liberated chloride ion. A potentiometric titration like that of Rudberg[7] was used.

> The apparatus was a Leeds and Northrup student type potentiometer and lamp-and-scale portable galvanometer, connected to a mercury-mercurous sulfate half-cell, a potassium sulfate bridge, and a silver-silver chloride half-cell. See Fig. 3.
> Standard silver nitrate solution was added from a microburet, and the electromotive force was measured and plotted against each addition of silver nitrate. The potential is given by
> $$E = E_0 + \frac{RT}{F} \ln \frac{(SO_4^=)^{\frac{1}{2}}}{(Cl^-)}$$
> if the liquid junction potential is neglected. The plot is a curve of the usual type, with the endpoint at the point of maximum slope. See Fig. 4. It was not necessary to pick this point exactly, as is explained below.

Since chloracetic acid undergoes a slow thermal hydrolysis, an unilluminated portion of the actinometer solution was titrated as a blank. The two curves have the same slope, so that the distance between them does not vary greatly near the endpoint. This distance is, accordingly, easily measured, and is a measure of the extent of the photo-hydrolysis.

> The standard silver nitrate solution was prepared by dissolving a known weight of pure, dry crystals, and diluting to concentrations of 0.05 n. and 0.005 n. A 0.1 n. solution of hydrochloric acid was prepared by standardization against sodium carbonate. Portions of this acid were then titrated potentiometrically as

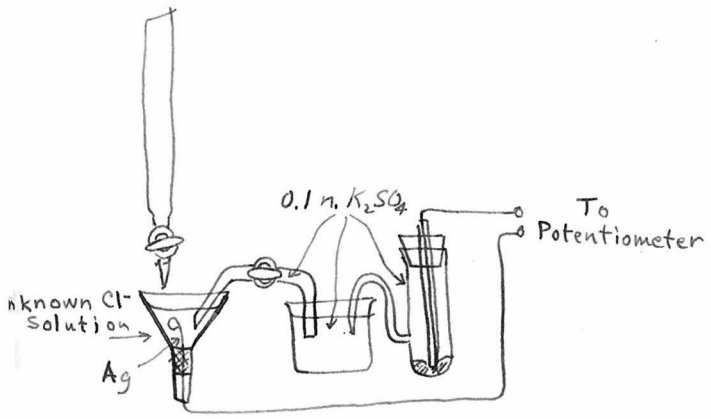


FIG. 3 TITRATION APPARATUS

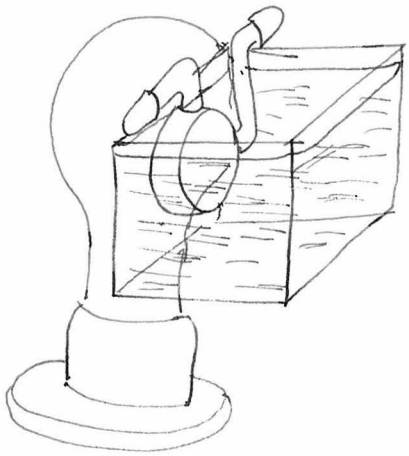


FIG. 6. ILLUMINATION FOR PURITY TEST.

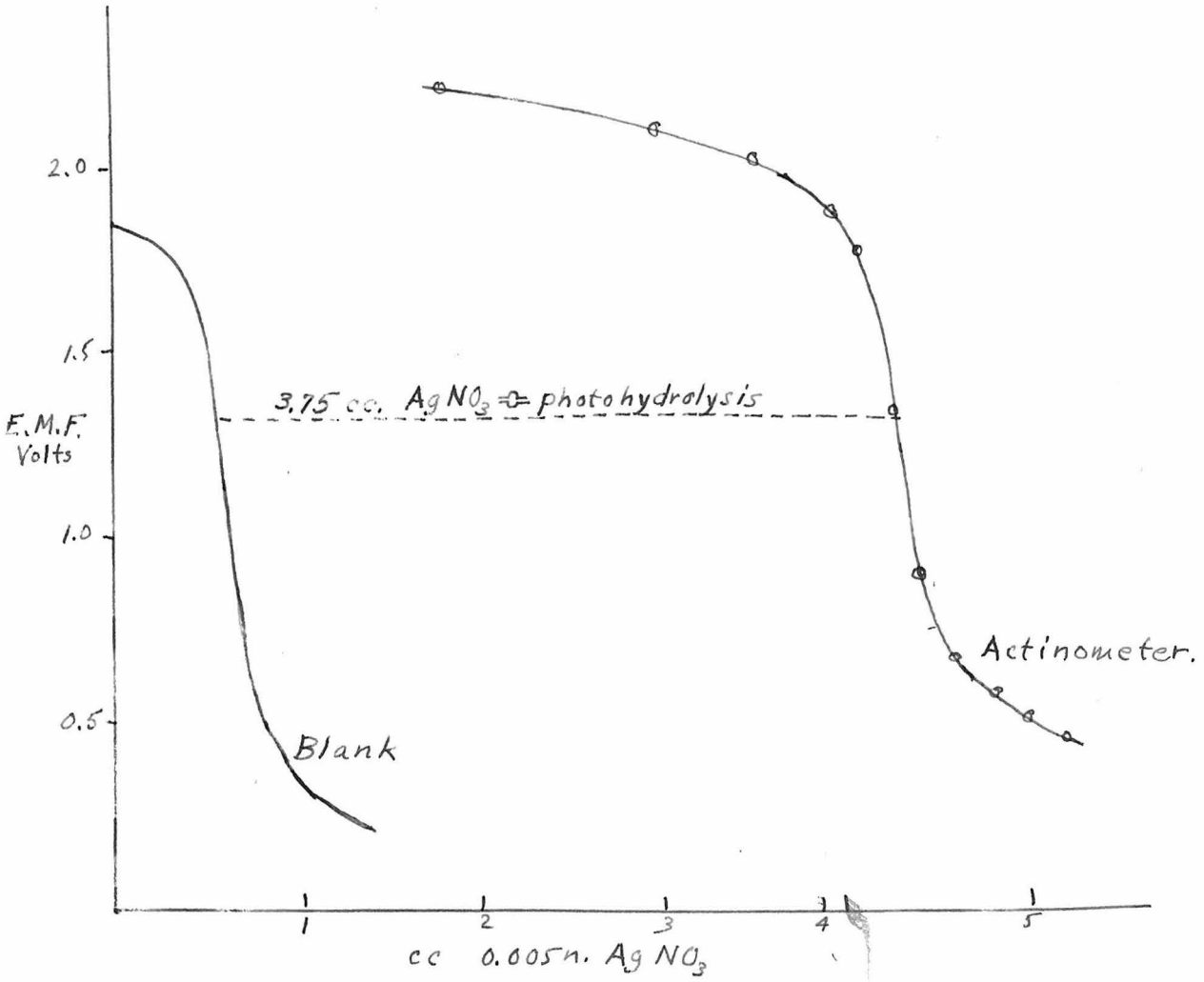


FIG. 4. TYPICAL TITRATION CURVES.

a check on the functioning of the potentiometer, and gave correct results within 0.7%. The same acid was used in standardizing the thiosulfate solutions. The concentrations were checked occasionally.

The chloracetic acid was Kahlbaum's technical preparation, distilled three times in an all glass still, the fractions boiling between 184° and 187° being accepted. The acid was kept in a desiccator and made up in 0.5 n. solutions immediately before use.

The light source was a quartz mercury-vapor arc. The mercury reservoir was water-cooled, and a magnet was provided to deflect the arc against the wall of the lamp, to prevent reversal of the 2537 ångstrom line by cool mercury vapor. The current was usually about 4.0 amperes.

The first few runs showed the necessity of using the purest carbon tetrachloride. The following standard test for purity was adopted: A dry five milliliter sample of the carbon tetrachloride to be tested was placed in a flat-walled, pyrex glass cell one centimeter thick. The cell, in a tank of running water, was placed three centimeters from a 500 watt tungsten lamp, as in Fig. 6. After a three-hour illumination, the sample was

shaken with water, and potassium iodide was added. The iodine liberated was titrated with thiosulfate. This eliminated the chlorine. The solution was boiled to drive off any carbon dioxide, as this was found to interfere with the measurement of the acidity. After the solution was cooled, potassium iodate was added, and the liberated iodine was titrated as a measure of the acid developed by the illumination:

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

It was felt that perfectly pure carbon tetrachloride should develop no acidity, but no sample satisfied this requirement. The following is an example of the procedures used on each preparation:

Treatment:	cc. 0.011 n. $Na_2S_2O_3$ required for acid in the standard test sample.
1. Untreated Merck's C.P. CCl_4	1.8 cc.
2. Saturate with pure Cl_2, illuminate 15 hours with 500 watt lamp, wash with KOH, H_2O, distill, dry over $CaCl_2$, and test	2.1 cc.
3. Same as 2, but illuminate 23 hours . .	1.6 cc.
4. Same as 2, but illuminate in strong sunlight for 21 hours	1.1 cc.
5. Repeat 4	1.5 cc.
6. Saturate with ClO_2, boil off, wash with KOH, then H_2O, dry, distill . .	1.0 cc.
7. Repeat 6	1.3 cc.
8. Repeat 6, but illuminate until ClO_2 is destroyed (about.90.min.). . .	0.5 cc.
9. Repeat 8, ...	0.4 cc.
10. Repeat 8	0.4 cc.

11. Saturate with both ClO_2 and Cl_2, then repeat 2 , , , , , , . 1.2 cc.
12. Saturate with ClO_2, illuminate until decolorized; repeat 10 times, thus building up a considerable concentration of Cl_2; finish as in 2 . . . . . 0.2 cc.

Morton[3] stresses the necessity of using pure carbon tetrachloride, but fails to mention an effective method, or any test of purity other than the spectroscopic test of Massol and Faucon[9] for carbon disulfide, which these experiments have shown to be inadequate. Benrath and Hertel[1] mention this difficulty in purification, however; their chlorine and nitric acid treatment proved to be ineffective, as did the chromic acid treatment often recommended.

All the carbon tetrachloride used in these experiments required 0.20-0.35 cc. 0.011 n. thiosulfate in the standard test described above, except that runs 1 and 2 were made with untreated C.P. material.

After the illumination, the carbon tetrachloride was shaken with water, and potassium iodide added. In some cases, the carbon tetrachloride was shaken directly with a potassium iodide solution. The liberated iodine was titrated with thiosulfate as

a measure of the oxidizing power developed by the illumination. As in the analysis of the sample in the test for purity, the solution was then boiled and cooled, and potassium iodate was added. After ~~the~~ the solution had stood ten minutes, the liberated iodine was titrated as a measure of the acid present.

> The thiosulfate solution was standardized by adding an excess of potassium iodide and iodate to a known portion of the standard hydrochloric acid mentioned above, and titrating the liberated iodine with the thiosulfate. It was also checked against standard dichromate and permanganate solutions.

The carbon tetrachloride was freed from oxygen by boiling it, at the same time bubbling nitrogen through it. The reaction flask was sealed while nitrogen was still streaming through the neck. It was found that the tank nitrogen was not entirely freed of oxygen by passing it over hot copper; it was accordingly bubbled through a cuprous ammonia solution which was continuously regenerated by being flowed over metallic copper. The nitrogen was then washed in a permanganate solution and dried by bubbling it through concentrated sulfuric acid. After this treatment, the nitrogen could bubble steadily through an

alkaline pyrogallol solution for thirty minutes without perceptibly darkening it. This was at least twice as much nitrogen as was used in the treatment of the carbon tetrachloride and the sealing of the flask. This pure nitrogen was used beginning with run 13.

Table 2 shows the results of all the runs made without oxygen. Beginning with run 13, the yield of chlorine is zero; and this is evidently due to the use of oxygen-free nitrogen. Beginning with run 14, especial pains were taken to dry the carbon tetrachloride as completely as possible, except in run 16, where a water phase was present during the illumination. With the exceptions of runs 16 and 20, no acid was formed in the illuminations. Run 16 was known to be wet; but run 20 can be explained only by assuming that some of the phosphorus pentoxide dryer was not entirely removed before the sample was analyzed, and, reacting with the water in the analysis, gave phosphoric acid. Runs 15, 17-19, 21-26, and 47 give sufficient evidence that when carbon tetrachloride is pure, free from oxygen, and dry, 2537 ångstrom light does not decompose it. Any possibility of a negative catalytic

effect of the dryer, which was present in most of the runs, is eliminated by using three different dryers, and by two runs without any dryer present.

The effect of water suggests the reaction

$$CCl_4 + H_2O \longrightarrow COCl_2 + 2HCl$$

which is known to occur at higher temperatures, and may be induced by ultra-violet light. Water is 0.01% soluble in carbon tetrachloride[10], and if the twenty-one milliliter sample of carbon tetrachloride used in the illuminations were saturated, it would accordingly contain 0.00019 equivalents. This is ample to account for the yields of acid obtained.

A complete tabulation of the data for the runs in the presence of oxygen is given in Table 3. Beginning with run 27, the form of apparatus shown in Fig. 1B was used. After standing for several hours over anhydrone in the side-arm of the flask, the carbon tetrachloride was poured through the filter to the quartz flask; the flask did not have to be opened to the air, and all danger of absorption of atmospheric moisture was thereby eliminated. However, it was not felt that the dryer was removed sufficiently from the carbon tetrachloride, and beginning with run 34, the flask shown in Fig. 1C was used.

This flask was filled by means of a vacuum distillation. A distilling flask was provided with a long side-arm which would extend through the gas reservoir to the quartz flask. It was filled with anhydrone and carbon tetrachloride, and allowed to stand sealed for several hours. Then the tip of the side-arm was broken and inserted into the reaction flask, which had previously been carefully dried. The joint between the side-arm and the gas reservoir was sealed by wiring on a short piece of rubber tubing. A vacuum pump was connected through a calcium chloride tube to the side-arm of the reaction flask, and the pressure reduced until the carbon tetrachloride boiled gently at 35-40°. It then distilled into the reaction flask, about half the carbon tetrachloride being lost as vapor in the process. After the distillation, a stream of dried oxygen was run through the apparatus. The distilling flask was then partially withdrawn, and the reaction flask sealed off.*

In run 46, the flasks were left open to the air through calcium chloride tubes, and the dis-

* During the runs, the carbon tetrachloride was shaken hourly to keep it saturated with oxygen.

tillation was made rapidly at atmospheric pressure. The results showed agreement only when the vacuum distillation was used; probably some impurity is removed thereby. Run 51 turned turbid; evidently some water was present.

In runs 31-39, the sample was split, and a portion was analyzed for chloride ion.

> The oxidizing agent was assumed to be chlorine, and was destroyed by adding ammonia, boiling, and acidifying. The chloride was determined by potentiometric titration with silver nitrate just as in the case of the actinometer. From the analysis of the other portion of the sample, the amount of chloride ion resulting from the chlorine was calculated, and subtracted from the total chloride ion found.

The amount of chloride ion checked closely with the acid and oxidizing agent produced.

After run 36, the window of the filter tank was found to be dirty, and the quantum yield is accordingly unreliable. This may also explain the high quantum yield in run 35.

Runs 34-45, 50, 52-57 show that an oxidizing agent (chlorine) and hydrochloric acid are produced in equivalent quantities, and the quantum yield appears to be quite close to two. The success of the analysis for chloride ion, assum-

ing the oxidizing agent to be chlorine and correcting therefor, as well as the deep yellow color developed in the longer runs, are evidence that the oxidizing agent is actually chlorine.

A mechanism in harmony with these facts is:

$$CCl_4 + h\nu \longrightarrow CCl_3 + Cl$$

If no oxygen is present, recombination occurs:

$$CCl_3 + Cl \longrightarrow CCl_4$$

If oxygen is present, oxidation occurs, possibly in this manner:

$$CCl_3 + O_2 \longrightarrow COCl_2 + ClO$$
$$ClO + ClO \longrightarrow Cl_2 + O_2$$
$$Cl + Cl \longrightarrow Cl_2$$

Summary.

1. It has been shown that carbon tetrachloride is not decomposed by light of wavelength 2537 ångstroms.

2. It has been shown that light of wavelength 2537 ångstroms produces an oxidation of carbon tetrachloride according to the reaction

$$CCl_4 + \tfrac{1}{2} O_2 \longrightarrow COCl_2 + Cl_2$$

It has been shown that one molecule of carbon tetrachloride is decomposed per quantum of light absorbed. A possible mechanism for this reaction

has been given.

3. The difficulty of purifying carbon tetrachloride for photochemical work has been pointed out.

4. Evidence suggesting a photochemical hydrolysis of carbon tetrachloride has been given.

Pasadena, California.
September 25, 1933.

Table 2. RUNS WITH PURE CARBON TETRACHLORIDE.

Run	Time (min.)	Einsteins x 10^5	Equiv. Cl_2 x 10^5	Equiv. acid x 10^5	Notes
1	120	5.8	0.00	5.6	Preliminary
2	150	6.2	1.1	0.0	Preliminary
8	200	2.8	2.3	6.6	Oxygen present
9	90	3.9	1.3	0.0	Oxygen present
10	270	10.2	0.20	1.5	Oxygen present
11	60	1.58	0.40	0.40	Oxygen present
12	120	3.38	0.60	0.18	Oxygen present
13	240	4.00	0.00	4.00	Pure N_2 used; wet
14	120	1.95	0.00	0.07	No O_2; nearly dry
15	240	4.10	0.00	0.02	No O_2; nearly dry
16	120	1.88	0.00	2.06	Water phase present
17	120	2.03	0.00	trace	Dried over P_2O_5
18	120	2.07	0.00	trace	P_2O_5 present
19	240	3.67	0.00	trace	P_2O_5 present
20	120	1.88	0.00	11.8	P_2O_5 present
21	180	2.93	0.00	0.00	Anhydrone present
22	240	3.78	0.00	0.00	Anhydrone present
23	150	2.60	0.00	0.00	Anhydrone present
24	180	2.80	0.00	trace	No drier present
25	120	2.18	0.00	0.00	Anhydrone present
26	120	2.06	0.00	0.00	$CaCl_2$ present
47	420	8.91	0.00	0.00	Vacuum distillation

Table 3. RUNS WITH PURE CARBON TETRACHLORIDE AND OXYGEN.

Run	Time (min.)	Einsteins x 10^5	Eq. Cl_2 x 10^5	Eq. acid x 10^5	Eq. Cl^- x 10^5	Quantum yields Cl_2	Quantum yields acid	Notes
3	120	6.2	1.37	14.6		0.22	2.34	Preliminary
4	10	1.1	0.82	0.50		0.82	0.49	Moist; turbid
5	60	5.4	1.43	15.56		0.26	2.88	Moist; turbid
6	150	13.6	3.43	69.0		0.25	5.08	Dried by Na
7	120	10.8	0.92	49.3		0.08	4.60	Water present
27	180	1.9	0.23	8.6		0.12	4.5	Anhydrone present
29	180	1.9	3.20	20.5		1.68	10.8	Anhydrone present
31	360	25.7	123.3	136.0	111.7	4.94	5.25	Anhydrone present
32	270	21.0	95.2	108.1	94.1	4.53	5.15	Anhydrone present
33	180	5.6	8.5	27.0	6.9	1.52	4.82	Anhydrone present
34	360	48.2	92.1	93.2	93.0	1.91	1.94	Vacuum dist.
35	270	38.1	85.1	85.4	85.4	2.23	2.28	Vacuum dist.
36	270	22.1	63.4	63.9	63.8	2.87	2.88	Windows dirty
37	300	24.1	47.6	48.0	48.0	1.98	1.99	Vacuum dist.
38	360	50.3	112.0	110.3	109.9	2.18	2.16	Vacuum dist.
39	400	12.1	23.5	23.7	21.3	1.95	1.96	Vacuum dist.
45	360	17.7	36.5	37.6		2.06	2.11	Vacuum dist.
46	360	37.6	26.5	17.7		0.70	0.48	No vacuum dist.
50	360	24.6	49.5	49.1		2.02	2.00	Vacuum dist.
51	300	11.1	22.1	11.5		1.99	1.04	Turbid
53	240	11.1	21.0	21.5		1.91	1.95	Vacuum dist.
54	120	10.0	20.0	19.7		2.00	1.97	Vacuum dist.
55	500	19.9	38.8	38.2		1.95	1.93	Vacuum dist.
56	210	9.6	19.0	18.9		1.98	1.95	Vacuum dist.
57	240	11.4	22.9	22.3		2.02	1.95	Vacuum dist.

Runs made without vacuum distillation are not considered significant.

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